

Standard Reference Materials:

**Hydrogen Cyanide H¹³C¹⁴N Absorption Reference for 1530–1560 nm
Wavelength Calibration – SRM 2519**

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ABSTRACT

Standard Reference Material (SRM) 2519 is an optical-fiber-coupled absorption cell containing hydrogen cyanide (H¹³C¹⁴N) gas. It is intended for use in calibrating the wavelength scale of wavelength measuring instruments in the 1500 nm region. About 50 accurately measured absorption lines of the R and P branch of the 2ν₃ rotational-vibrational band of H¹³C¹⁴N are located in the 1530-1560 nm region. We have measured the line centers and pressure-induced shifts of 21 lines and certify their wavelengths with an expanded uncertainty (coverage factor $k = 2$) of ± 0.0006 nm. The remainder of the lines in the band are certified with an expanded uncertainty of ± 0.003 nm. This publication describes the SRM, the NIST measurement procedure, and the uncertainty determination for SRM certification.

Keywords: absorption; hydrogen cyanide; molecular spectroscopy; optical fiber communication; Standard Reference Material; wavelength calibration; wavelength division multiplexing; wavelength reference; WDM

1. Introduction

Wavelength references are needed in the 1500 nm region to support future wavelength division multiplexed (WDM) optical fiber communication systems. In a WDM system, many wavelength channels are sent down the same fiber, thereby increasing the bandwidth of the system by the number of channels. If one channel's wavelength were to shift, crosstalk could occur between it and a neighboring channel. Wavelength references are needed to calibrate instruments that characterize system components and measure the channel wavelengths.

Most applications involve calibrating a commercial optical spectrum analyzer (OSA) which is based on the dispersion of light by a diffraction grating. An OSA typically has a resolution of 0.1 nm; the highest resolution currently available is 0.05 nm. Most users are interested in calibrating these instruments to an uncertainty between 0.1 and 0.01 nm. Many users are also interested in calibrating the wavelength scan linearity of their instruments. A calibration service did not seem practical for these instruments; they are large and fragile, and the optical elements can shift during shipment, causing a loss of wavelength calibration. The NIST solution is to produce Standard Reference Material (SRM) cells containing gases which have accurately measured absorption lines in this wavelength region. Fundamental molecular absorptions provide references that are very stable under changing environmental conditions such as temperature and pressure variations, or the presence of electric and magnetic fields. These SRMs can also be used to calibrate the wavelength readout of tunable lasers and check the accuracy of wavelength meters.

There are very few wavelength references available in the 1500 nm region. There is only one gas laser reference line: the 1523 nm helium-neon laser. The only atomic absorption lines in this region are between excited states and thus require initial excitation by a laser or electric discharge. Another possibility is frequency doubling 1500–1560 nm light to probe atomic transitions in the 750–780 nm region. This requires fairly complicated and expensive apparatus. Molecular transitions in the 1500 nm region are combination or overtone bands that can be probed directly.

We have chosen to use the absorption lines of acetylene (SRM 2517) and hydrogen cyanide (this SRM) for references in the 1500 nm region for the following reasons:

- (1) Molecular lines are simple to access, since this involves simply passing light through a cell containing the gas and observing the absorption spectrum.
- (2) These molecules have strong absorption bands in this region.
- (3) The combined spectra of the two gases cover the communications band, from 1510 to 1565 nm.
- (4) The spectra are uncomplicated; thus it is not difficult to identify the lines.
- (5) The wavelengths of the prominent lines have been measured with an uncertainty of less than 0.001 nm.
- (6) There are many reference lines with spacings ranging from 0.4 to 0.9 nm, providing for scan linearity calibration as well as single-point wavelength calibration.

- (7) A cell containing the gas can be easily pigtailed with optical fiber, so that it is compatible with the sources and measurement instruments used by the optical fiber communications industry.
- (8) The gas cell design allows for versatile calibration capability; it can be used with a variety of sources (LED, amplified spontaneous emission, white light, laser, etc.) to calibrate any wavelength measuring instrument in this region.

2. SRM 2519 description

SRM 2519 is based on the fundamental absorption of light by hydrogen cyanide ($\text{H}^{13}\text{C}^{14}\text{N}$). The spectrum of this molecule in the 1500 nm region is shown in Fig. 1. The lines are the R and P branches of the $2\nu_3$ rotational-vibrational band of $\text{H}^{13}\text{C}^{14}\text{N}$. Figure 2 shows a schematic diagram of our apparatus for measuring the spectrum in Fig. 1. Light from an LED source (about 80 nm bandwidth) is coupled to a hydrogen cyanide absorption cell using single-mode optical fiber. The light exiting the fiber is collimated by a lens, passes through the absorption cell three times, and is coupled into another section of single-mode fiber. This fiber is connected to a commercial optical spectrum analyzer. The resulting spectrum is the emission spectrum from the LED with narrow depressions due to the absorption of the light by the molecules. The spectrum in Fig. 1 has been normalized to the LED spectrum. We have also recorded the spectrum using a tunable laser as the light source. In this case, the transmission through the cell was monitored by a detector as the laser's wavelength was tuned.

The vacuum wavelengths of the hydrogen cyanide $2\nu_3$ lines have been measured with a quoted uncertainty of 0.00012 nm [1]. Table 1 lists these literature values for the wavelengths from 1527 to 1565 nm. Also shown in Table 1 are NIST measurements of selected lines obtained using line center measurements at different pressures and extrapolating to zero pressure. With the exception of line R23, the measurements agree within the NIST expanded uncertainty of ± 0.0004 nm. Reference [2] states that R23 is a "blended line." This additional structure (ie. additional absorption line(s)) is the likely cause of the difference between our measurement and the measurement reported in Ref. [1].

3. SRM design

The SRM design is essentially that shown schematically in Fig. 2; an absorption cell (7.5 cm long) is pigtailed with single-mode optical fiber. To increase the absorption depth, light is passed through the cell three times by reflecting it off mirrors mounted within the cell housing. The cell housing is mounted inside an instrument box; input and output ports on this instrument box are FC/PC optical fiber bulkhead connectors. Users supply their own light source and detection; this enables flexibility since some users may want to calibrate optical spectrum analyzers using a broadband light source, and others may want to check the calibration of tunable lasers or wavelength meters using a narrowband source.

The absorption cell material is fused silica; the windows are fused to the cell using a glass frit method. To prevent interference fringes in the transmitted signal, the windows are mounted at an angle of 11° and are also wedged by about 2° . The cell is first evacuated and leak-checked, and

then filled with high purity $\text{H}^{13}\text{C}^{14}\text{N}$ gas. Once the cell is filled, it is tipped off using a torch, providing an all-glass seal. The cell is securely mounted in an aluminum holder. The fiber-coupled collimators are also mounted on this holder using commercially available aligners.

We chose an HCN pressure of 13 kPa (100 Torr) so that the lines are pressure-broadened by less than 0.1 nm and thus provide a large signal, without significant loss of resolution, when used with instruments with this resolution. At this pressure, there is a slight shift of each line (pressure shift) due to energy level shifts caused by the interaction of the molecules during collisions [3]. Pressure shifts ranging from +1.6 to +2.3 MHz/Torr (12 to 17 MHz/kPa) have been reported for the P20, P23, P24, and P27 lines of the $2\nu_3$ band of $\text{H}^{13}\text{C}^{14}\text{N}$ [1]. We have measured the pressure shift for 21 different lines, as described in section 4.1.

4. Line center uncertainty

For this Standard Reference Material, the stability of the wavelength of each absorption line is a critical characteristic. The choice of fundamental molecular absorption lines makes the SRM insensitive to most changes in environmental conditions. For the desired SRM certification uncertainty of about 0.001 nm, the only line shift mechanism which could potentially contribute at this level is the shift due to pressure (collisions between molecules). Other factors associated with line fitting could cause apparent shifts of lines. In section 4.1 we discuss our measurement of the pressure shift.

4.1 Pressure shift measurement

A schematic diagram of our pressure shift measurement apparatus is shown in Fig. 3. Light from a tunable diode laser is sent through two absorption cells simultaneously, and the transmission through each cell is monitored by a detector. Both cells are 15 cm long; one cell contains hydrogen cyanide gas at low pressure (1.3 ± 0.1 kPa; about 10 Torr) and the other contains a higher pressure of 12.6 ± 0.7 kPa (about 95 Torr). The pressure uncertainty quoted is the expanded uncertainty using a coverage factor $k = 2$ (i.e. our quoted uncertainty is $\pm 2\sigma$) [4]. A wavelength meter with an uncertainty of 1 part in 10^7 (0.00016 nm) monitors the wavelength of the laser. A computer scans the wavelength of the laser in approximately 0.001 nm steps and records the readings of the two detectors and the wavelength meter.

Figure 4 shows the spectrum obtained of line P11. The pressure broadening in the high-pressure cell is obvious. We are interested in the relative shift between the line centers in the low-pressure and high-pressure cells. Twenty one lines were recorded using this technique. The measured quantity, the transmitted power I_T , is related to the absorption coefficient \mathbf{a} and the absorption path length L by

$$I_T = I_o \exp(-\mathbf{a}L), \quad (1)$$

where I_o is the incident power. We first normalized the data to I_o and then took the natural logarithm to obtain $\mathbf{a}L$. The low pressure lines were fitted to a Voigt profile [5] using an orthogonal distance regression algorithm [6]. The orthogonal distance regression, called either

error-in-variables or total least squares regression, obtains the model parameters (Voigt profile parameters in this case) by minimizing the sum of squares of the orthogonal distances from the model to the data points. Due to the dominance of pressure broadening in the high pressure cell, these lines were fitted to a Lorentzian profile. Several factors complicated the fitting procedure: overlap with nearby lines, background slopes, and occasional outlying data points. Our approach to minimizing and measuring the effects of these contributions is discussed below.

4.1.1 Overlap with nearby lines

Wings of nearby lines can skew the shape of the line being measured and shift its apparent center. In addition to the strong lines of the $2\nu_3$ band, there are a number of weak lines throughout the spectrum which are due to hot bands (transitions that are not out of the ground vibrational state) [1, 2]. To minimize the effect of weak neighboring lines on our pressure shift measurement, we deliberately avoided measuring lines in the spectrum that had weak lines very close to the primary line. To estimate the effect of weak nearby lines on the lines that we did measure, we chose to do a detailed analysis of P4, the line that was affected the largest amount due to the proximity of weak neighboring lines. We did a multiple-line fit to the low pressure spectrum of line P4 and then used the line locations and strengths obtained in this fit as input to a multiple-line fit of the high pressure spectrum. A multiple-line fit is simply a fit to a sum of lines instead of a single line. After modeling the weak lines, we subtracted them from the data to obtain a spectrum that contained only the main line. This modified spectrum could then be fit more accurately with the appropriate error bars. We found that the removal of these weak lines caused a negligible shift in the P4 line center for the low pressure cell data and a 0.00003 nm shift for the high pressure data. Assuming a rectangular distribution with upper and lower limits of ± 0.00003 nm about the mean value, this corresponds to a standard uncertainty (estimated standard deviation) u of 0.00002 nm ($= 0.00003/\sqrt{3}$).

We also conducted a similar analysis to determine the effect of the wings of the neighboring lines of the main ($2\nu_3$) band. Although these lines are relatively far apart, there is a slight overlap, particularly in the R branch. We chose R3 for this analysis, since it is located in a region where there is a noticeable background slope due to the overlap of the lines. We modeled adjacent lines R2 and R4 using Lorentzian profiles with the appropriate depth, width, and center wavelengths obtained from separate scans of these lines. We then subtracted the background due to these lines from the data in the vicinity of R3. This resulted in a negligible shift of the R3 line center for both the low and high pressure data.

4.1.2 Background slope

A slope in the background level can shift the apparent center of a line, particularly for the wide lines of the high pressure cell. We have identified two sources of background slope: (1) wavelength dependence of the fiber couplers (splitters) and other optical components, and (2) change in the laser power. To remove the background slope, we took background scans of each channel with the cells removed. The background slope was then fitted with a linear or quadratic function and the scan data was divided by this function. After this procedure, slight residual slopes in the data could be seen in the fit residual plots. By fitting the data again with the residual slope removed, we calculate that the maximum shift due to any residual slope is negligible for the

low pressure cell data and 0.00015 nm for the high pressure cell data. Assuming a rectangular distribution with upper and lower limits of ± 0.00015 nm about the mean value, this corresponds to a standard uncertainty u of 0.00009 nm.

4.1.3 Outlier point removal

Some data sets contained a few points that were well outside of the normal variation ($\gg 3\sigma$ away from the line fit). These points usually occurred in the vicinity of a laser mode hop. Since we were not able to measure the laser wavelength and the transmission through the cells exactly simultaneously, the measured wavelength could differ from the actual wavelength at the time of the transmission measurements. We removed the most distant outlying points in these cases and found that the point removal resulted in a maximum line center shift of 0.00003 nm for the high pressure cell and 0.00005 nm for the low pressure cell. Assuming a rectangular distribution with upper and lower limits of ± 0.00003 nm and ± 0.00005 nm about the mean value, this corresponds to a standard uncertainty u of 0.00002 and 0.00003 nm respectively.

4.1.4 Line fitting statistics and reproducibility

The fitting program was able to account for uncertainty in both x (wavelength) and y (transmitted power). We determined the uncertainty in transmitted power by measuring the statistical variation of the data within a region of the line wing. Since the transmissions through the low and high pressure cells were measured simultaneously, the absolute accuracy of the wavelength meter was not of critical importance for the relative pressure shift measurement. However, the short term statistical variation of the wavelength measurement did add noise to the data. To determine this statistical variation, we took repeated measurements of a stable laser wavelength over a short time period and derived a standard uncertainty of 0.0001 nm. Both the transmitted power uncertainty and the wavelength uncertainty were incorporated into each line fit. The program assigned an uncertainty to the line center determination based on the goodness of fit. This uncertainty ranged from 0.00001 to 0.00005 nm for the different lines. The fit residual plots revealed non-white noise which could potentially cause additional uncertainty in the line center. We used a first-order autoregressive (AR) process [7] to model this noise and conducted a simulation to study the effect of the noise on the line center uncertainty estimate. A set of 5000 points representing a typical high pressure line was generated. Values of y (transmitted power) were perturbed by the disturbance from a first-order AR process. We used a random sample of 250 points in the fitting program to obtain the line center and its uncertainty. The procedure was repeated 1000 times. By comparing the root-mean-square error of the 1000 center estimates and the uncertainties output from the program, we found that the effect of the non-white noise was to increase the statistical uncertainty by about 20%. From this we assign an average fit statistical uncertainty of 0.00004 nm.

To test the reproducibility of the line fit, we took several scans on the same lines and determined the pressure shift for each scan. Since the wavelength meter could drift slightly between each scan, we could only compare the shift measurement, not the individual measurements for the low and high pressure cells. We found that the shift values for six lines changed by a maximum of 0.00024 nm. Assuming a rectangular distribution with upper and lower limits of ± 0.00024 nm about the mean value, this corresponds to a standard uncertainty u of 0.00014 nm. Since this is

an uncertainty in the shift measurement, not the individual line centers, we then divide this value by $\sqrt{2}$ and assign a standard uncertainty of 0.00010 nm each for the low pressure and high pressure cell data.

4.1.5 Pressure shift results

We measured the pressure shifts for 21 different lines, choosing lines at a variety of locations in the spectrum. This ensured that our data would be sensitive to any variations in the pressure shift, if the shift varied with line number. The uncertainty budget for the relative line center determinations is given in Table 2. With the exception of the Type A fit statistical uncertainty, all other uncertainty sources are Type B [4]. The combined standard uncertainty for the pressure shift measurement of each line is 0.00018 nm.

Table 3 shows the results of the pressure shift measurements. We found that the shift does have a large dependence on line number, ranging from -0.0017 nm (-1.5×10^{-4} nm/kPa, or equivalently $+19$ MHz/kPa) for line P16 to $+0.0012$ nm ($+1.1 \times 10^{-4}$ nm/kPa, or -14 MHz/kPa) for line P4. The R branch has a similar trend, with pressure shifts ranging from -0.0008 nm to $+0.0011$ nm. The pressure shifts near the center of each branch (near R9 and P9) are nearly zero. The overall trend is that lines in each branch (P or R) shift toward the center of that branch. We mapped out this behavior by choosing lines in all parts of the spectrum. To investigate the shift's pressure dependence in more detail, we also measured selected line shifts for two other pressures: 5.3 kPa and 53 kPa. Figure 5 shows the results of the pressure shift measurements of 3 lines. As expected, the shift is linear with pressure.

To our knowledge, the only previous pressure shift measurement in the $\text{H}^{13}\text{C}^{14}\text{N } 2\nu_3$ band is given in Ref. [1], where they report pressure shift measurements of lines P20, P23, P24, and P27 ranging from $+1.6$ to $+2.3$ MHz/Torr ($+12$ to $+17$ MHz/kPa). Our results are consistent with this; our measurements for lines P23 and P24 are $+15$ and $+16$ MHz/kPa respectively. From our data, we predict that the shifts would be the same sign and similar magnitude for P27 and slightly higher in magnitude for P20. Unfortunately, the researchers in Ref. [1] did not measure the pressure shift in other parts of the spectrum. A survey of the pressure shift was done on the $5\nu_3$ band of HCN [8]. In this case the measured pressure shifts were opposite in sign to those reported in Ref. [1] and considerable J-dependent variation was observed.

The large line dependence of the shifts may be due to collisional line mixing. HCN exhibits a large collisional line mixing effect, where collisions transfer coherence among transitions of overlapping lines [9]. This line mixing results in non-additivity of absorption lines as pressure broadening blends them together; the transitions can no longer be treated as independent absorption lines. The underlying physical basis for line mixing is inelastic collisions that transfer coherence from a given transition to another and then back again before the coherence is lost due to the different rate of precession. Dipole-dipole interaction between the highly polar HCN molecules leads to significant rotationally inelastic collisional cross sections even at long range. Research results presented in Ref. [8] suggest that rotationally resonant dipole collisions, where one molecule goes from J to $J+1$ and the other from $J+1$ to J , have large cross sections in HCN and dominate the pressure broadening. In Ref. [9], the authors speculate that strong line mixing

could lead to an enhanced pressure shift. Clearly, the study of the HCN pressure shift mechanism is an interesting area for further research.

4.2 Line center wavelength measurement

To determine the line center accuracy for our measurements on 21 lines, we first checked the accuracy of the wavelength meter used in the measurements. We have set up a high accuracy wavelength reference for this purpose. Diode laser light at 1560.5 nm is amplified using an erbium-doped fiber amplifier and frequency doubled in a periodically poled lithium niobate (PPLN) crystal. The resultant 780 nm light is then used to conduct saturated absorption spectroscopy on the $5S_{1/2} \rightarrow 5P_{3/2}$ transitions of rubidium (^{85}Rb and ^{87}Rb). The line centers of the hyperfine components of these transitions have been measured with an uncertainty of ± 0.4 MHz [10]. We stabilized the laser to several different hyperfine components of the ^{87}Rb transition and compared the wavelength meter reading to the literature values multiplied by 2. Since the lines were very narrow (less than 10 MHz), the absolute stability of the laser was much better than the quoted wavelength meter accuracy of 1 part in 10^7 (about 20 MHz at 1560 nm). We found that the wavelength meter reading was within 0.00010 nm of the literature values for the 6 lines measured. The statistical variation of repeated measurements on the same line yielded a Gaussian distribution with a standard deviation of 0.0001 nm.

Table 4 gives the uncertainty budget for determination of the absolute line centers for the conditions of very low pressure (extrapolated to zero pressure) and the 13.3 ± 2.7 kPa SRM conditions. The value for the wavelength meter uncertainty is the uncertainty specified by the instrument's manufacturer. Although our measurements showed that the wavelength meter can have higher accuracy than this over short time periods, the larger uncertainty can account for longer term variations. Due to the pressure shift, the pressure uncertainty in the SRM units (1 standard uncertainty = 10% of the pressure) leads to a 0.00020 nm standard uncertainty in the center wavelength.

The combined standard uncertainty of the line centers for the low pressure extrapolation (NIST measured lines given in Table 1) is 0.00019 nm, yielding an expanded uncertainty (coverage factor $k = 2$) of ± 0.00038 nm. The combined standard uncertainty of the line centers for the SRM conditions is 0.00029 nm, yielding an expanded uncertainty of ± 0.00058 nm.

4.3 Certified wavelength values

Unless otherwise stated, the uncertainties given below are all expanded uncertainties using a coverage factor $k = 2$. For each of the 21 lines measured in this work, we use our measured line centers at 12.6 kPa (from Table 3) and extrapolate them to the slightly higher SRM cell pressure of 13.3 kPa. We assign an uncertainty of ± 0.0006 nm to each of these line centers, as described in the previous section (the uncertainty budget is given Table 4).

For the remaining lines, we use the literature values for the line centers and assign a higher uncertainty due to the pressure shift variation observed throughout the spectrum. We determine this uncertainty by assuming a rectangular distribution of pressure shift values with a half-width given by the largest pressure shift possible at the SRM cell pressure. Our pressure shift results

range from -0.0017 ± 0.0003 nm (line P16) to $+0.0012 \pm 0.0003$ nm (line P4) for the 11.3 ± 0.7 kPa (85 ± 5 Torr) pressure difference. The largest shift (line P16) is $(1.5 \pm 0.3) \times 10^{-4}$ nm/kPa (2.0×10^{-4} nm/Torr), or equivalently 19 MHz/kPa (2.5 MHz/Torr). For the 13.3 ± 2.7 kPa (100 ± 20 Torr) pressure used in the SRM units, this pressure shift can be as large as 0.0024 nm at the upper end of the cell pressure range. Assuming a rectangular distribution with upper and lower limits of ± 0.0024 nm about the mean value, this corresponds to a standard uncertainty u of 0.0014 nm. With the coverage factor of 2, our expanded uncertainty for the remaining line centers is ± 0.003 nm. Table 5 lists the certified wavelengths for the SRM units.

5. HCN safety

We have conducted a literature study of hydrogen cyanide toxicity and have concluded that the small amount of HCN in each SRM unit (less than 1 mg) is not a safety concern. The current workplace exposure limit is 4.7 ppm (5 mg/m^3) for a period of 15 min. Although cyanide (CN) is toxic at higher concentrations, low concentrations are frequently found in normal human blood [11, 12]. Researchers estimate that normal blood cyanide levels are about 0.4 mg/l; smokers tend to have much higher levels [11]. Since the cyanide ion diffuses easily to all parts of the body, if a person were to inhale or ingest the entire contents of the SRM cell the resultant cyanide concentration would be less than the background level in normal human blood.

6. SRM 2519 certificate

The certificate for SRM 2519 is presented in Appendix A. It includes the certified wavelength values for the $2\nu_3$ band of $\text{H}^{13}\text{C}^{14}\text{N}$ ranging from R25 to P25 (1528-1563 nm), a scan of the band, and instructions for storage, handling, and use of the SRM.

7. Acknowledgment

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8. References

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Table 1. Vacuum Wavelengths of Hydrogen Cyanide $2v_3$ Lines

The wavelength uncertainty estimate given in Ref. [1] is 0.00012 nm. NIST measurements of selected lines were obtained using line center measurements at different pressures and extrapolating to zero pressure. The uncertainty of the NIST measurements is ± 0.00038 nm (expanded uncertainty using a coverage factor $k = 2$).

R Branch	wavelength from Ref. [1] (nm)	wavelength NIST meas. (nm)	P Branch	wavelength from Ref. [1] (nm)	wavelength NIST meas. (nm)
27	1527.2210		1	1543.1140	1543.1141
26	1527.6327		2	1543.8094	
25	1528.0541		3	1544.5147	
24	1528.4851	1528.4853	4	1545.2299	1545.2299
23	1528.9258	1528.9265	5	1545.9551	1545.9552
22	1529.3762		6	1546.6902	
21	1529.8363	1529.8367	7	1547.4354	
20	1530.3061		8	1548.1904	
19	1530.7856		9	1548.9555	1548.9553
18	1531.2749	1531.2752	10	1549.7305	1549.7305
17	1531.7738		11	1550.5156	1550.5157
16	1532.2825		12	1551.3106	
15	1532.8010	1532.8011	13	1552.1157	
14	1533.3291		14	1552.9308	
13	1533.8671		15	1553.7560	
12	1534.4148	1534.4150	16	1554.5912	1554.5912
11	1534.9723		17	1555.4365	1555.4365
10	1535.5396	1535.5398	18	1556.2919	
9	1536.1167	1536.1169	19	1557.1573	
8	1536.7036	1536.7035	20	1558.0329	
7	1537.3003	1537.3004	21	1558.9185	
6	1537.9069		22	1559.8143	
5	1538.5232	1538.5234	23	1560.7202	1560.7201
4	1539.1494		24	1561.6363	1561.6362
3	1539.7855		25	1562.5625	
2	1540.4314		26	1563.4989	
1	1541.0872		27	1564.4455	
0	1541.7529		28	1565.4022	

Table 2. Uncertainty Budget for Relative Line Center Determinations

Uncertainty budget for determination of relative line centers for the low pressure and high pressure cells. The combined standard uncertainties are root-sum-of-squares (RSS) of the standard uncertainties due to the sources listed. The absolute accuracy of the wavelength meter is not included since we are concerned only with the relative line centers. The individual line shift standard uncertainty $u_c(\mathbf{D})$ is the RSS combined uncertainty of $u_c(low)$ and $u_c(high)$.

Source of uncertainty	Standard uncertainty (nm) 1.3 kPa (<i>low</i>) cell	Standard uncertainty (nm) 13 kPa (<i>high</i>) cell
Nearby line contribution	< 0.00001	0.00002
Background slope	< 0.00001	0.00009
Outlier removal	0.00003	0.00002
Fit statistical uncertainty	0.00004	0.00004
Fit reproducibility	0.00010	0.00010
Combined standard uncertainty for relative line center	$u_c(low) = 0.00011$	$u_c(high) = 0.00014$
Combined standard uncertainty for pressure shift (each line)	$u_c(\mathbf{D}) = 0.00018$	

Table 3. Pressure Shift Measurement

Measured center wavelengths and pressure shifts for 21 lines of H¹³C¹⁴N. The combined standard uncertainty $u_c(\mathbf{D})$ for each line's pressure shift is 0.00018 nm.

Line	Measured center λ (nm) 1.3 kPa (<i>low</i>) cell	Measured center λ (nm) 12.6 kPa (<i>high</i>) cell	Shift (nm) [$\Delta = high - low$]	Shift nm/kPa $\times 10^5$
R24	1528.48542	1528.48617	+ 0.00075	+ 6.6
R23	1528.92658	1528.92709	+ 0.00051	+ 4.5
R21	1529.83679	1529.83759	+ 0.00080	+ 7.1
R18	1531.27536	1531.27633	+ 0.00097	+ 8.6
R15	1532.80121	1532.80234	+ 0.00113	+ 10.0
R12	1534.41507	1534.41581	+ 0.00074	+ 6.5
R10	1535.53982	1535.54012	+ 0.00030	+ 2.6
R9	1536.11688	1536.11698	+ 0.00010	+ 0.9
R8	1536.70352	1536.70336	- 0.00016	- 1.4
R7	1537.30035	1537.29977	- 0.00058	- 5.1
R5	1538.52328	1538.52246	- 0.00082	- 7.2
P1	1543.11417	1543.11481	+ 0.00064	+ 5.6
P4	1545.23007	1545.23132	+ 0.00125	+ 11.0
P5	1545.95529	1545.95629	+ 0.00100	+ 8.8
P9	1548.95533	1548.95542	+ 0.00009	+ 0.8
P10	1549.73046	1549.73021	- 0.00025	- 2.2
P11	1550.51561	1550.51497	- 0.00064	- 5.6
P16	1554.59101	1554.58933	- 0.00168	- 14.8
P17	1555.43634	1555.43471	- 0.00163	- 14.4
P23	1560.71994	1560.71862	- 0.00132	- 11.6
P24	1561.63605	1561.63453	- 0.00152	- 13.4

Table 4. Uncertainty Budget for Absolute Wavelength Determination

Uncertainty budget for determination of the absolute line centers of 21 lines for very low pressure (extrapolated to zero) and 13.3 ± 2.7 kPa SRM conditions. The combined standard uncertainties are the RSS of the standard uncertainties due to the sources listed.

Source of uncertainty	Standard uncertainty (nm) very low pressure	Standard uncertainty (nm) 13.3 kPa SRM cell
Standard uncertainty for relative line center (from Table 2)	0.00011	0.00014
Wavelength meter uncertainty	0.00016	0.00016
Pressure uncertainty	0.00002	0.00020
Combined standard uncertainty	0.00019	0.00029

Table 5 Certified Wavelengths for SRM 2519

The table lists the vacuum wavelengths of line centers in the $\text{H}^{13}\text{C}^{14}\text{N } 2\nu_3$ band for the 13.3 kPa (100 Torr) SRM cell pressure. The 21 lines that were measured at NIST are certified with an expanded uncertainty (coverage factor $k = 2$) of ± 0.0006 nm. These lines are shown in the table with a (6) indicating the uncertainty in the last digit. The remaining line centers listed are the literature values from Ref. [1]. These values are certified with an expanded uncertainty of ± 0.003 nm, where the uncertainty is dominated by the pressure shift uncertainty.

R Branch	wavelength (nm)	P Branch	wavelength (nm)
25	1528.054	1	1543.1148(6)
24	1528.4862(6)	2	1543.809
23	1528.9271(6)	3	1544.515
22	1529.376	4	1545.2314(6)
21	1529.8376(6)	5	1545.9563(6)
20	1530.306	6	1546.690
19	1530.786	7	1547.435
18	1531.2764(6)	8	1548.190
17	1531.774	9	1548.9554(6)
16	1532.283	10	1549.7302(6)
15	1532.8024(6)	11	1550.5149(6)
14	1533.329	12	1551.311
13	1533.867	13	1552.116
12	1534.4159(6)	14	1552.931
11	1534.972	15	1553.756
10	1535.5401(6)	16	1554.5892(6)
9	1536.1170(6)	17	1555.4346(6)
8	1536.7034(6)	18	1556.292
7	1537.2997(6)	19	1557.157
6	1537.907	20	1558.033
5	1538.5224(6)	21	1558.919
4	1539.149	22	1559.814
3	1539.786	23	1560.7185(6)
2	1540.431	24	1561.6344(6)
1	1541.087	25	1562.563
0	1541.753		

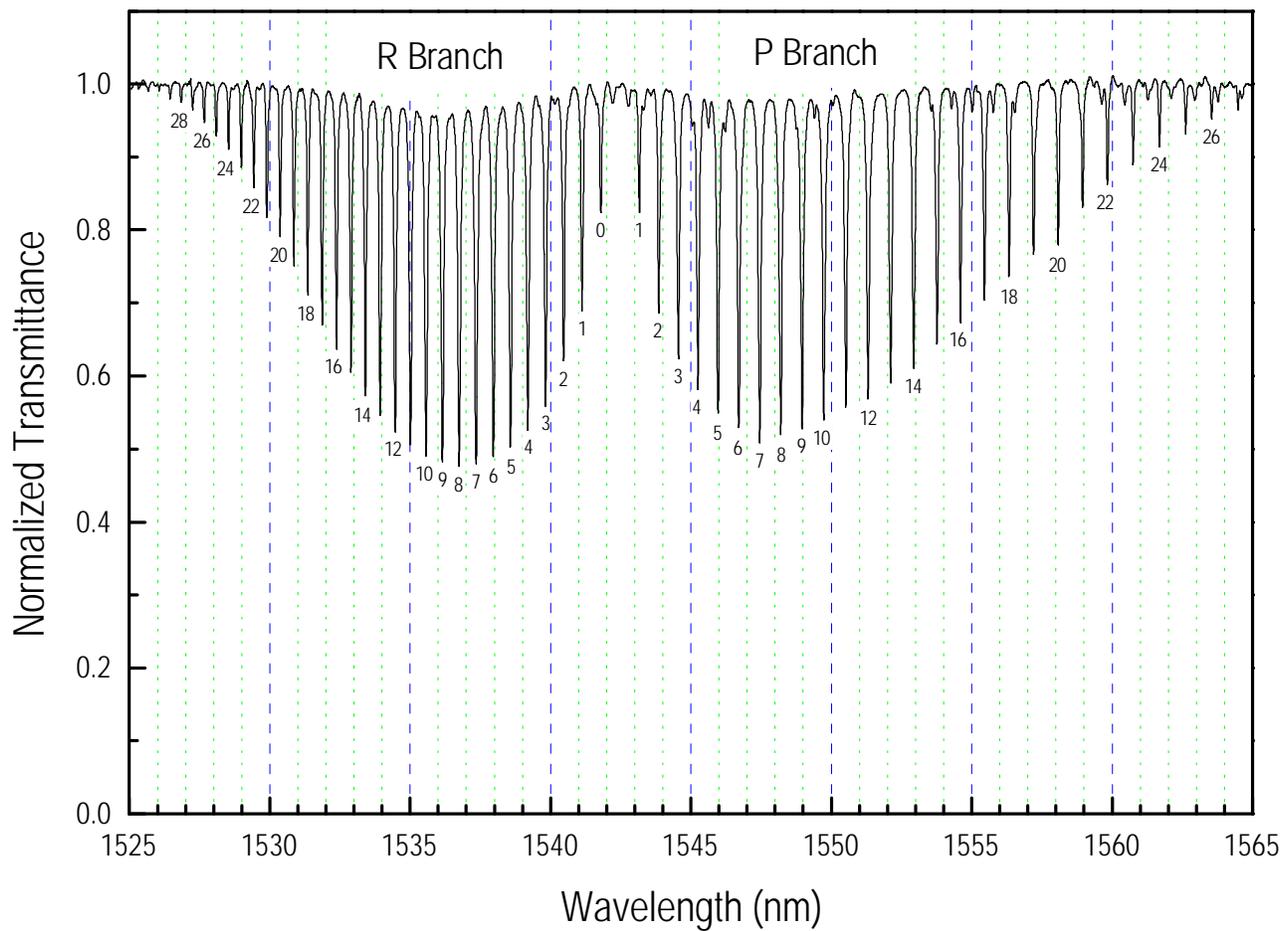


Figure 1. Hydrogen cyanide ($\text{H}^{13}\text{C}^{14}\text{N}$) spectrum taken by passing LED light through a SRM unit and recording the spectrum of the transmitted light using an optical spectrum analyzer with 0.05 nm resolution. The figure shows the recorded spectrum divided by the LED spectrum. The HCN gas pressure is 13 kPa and the optical path length through the gas is 22.5 cm.

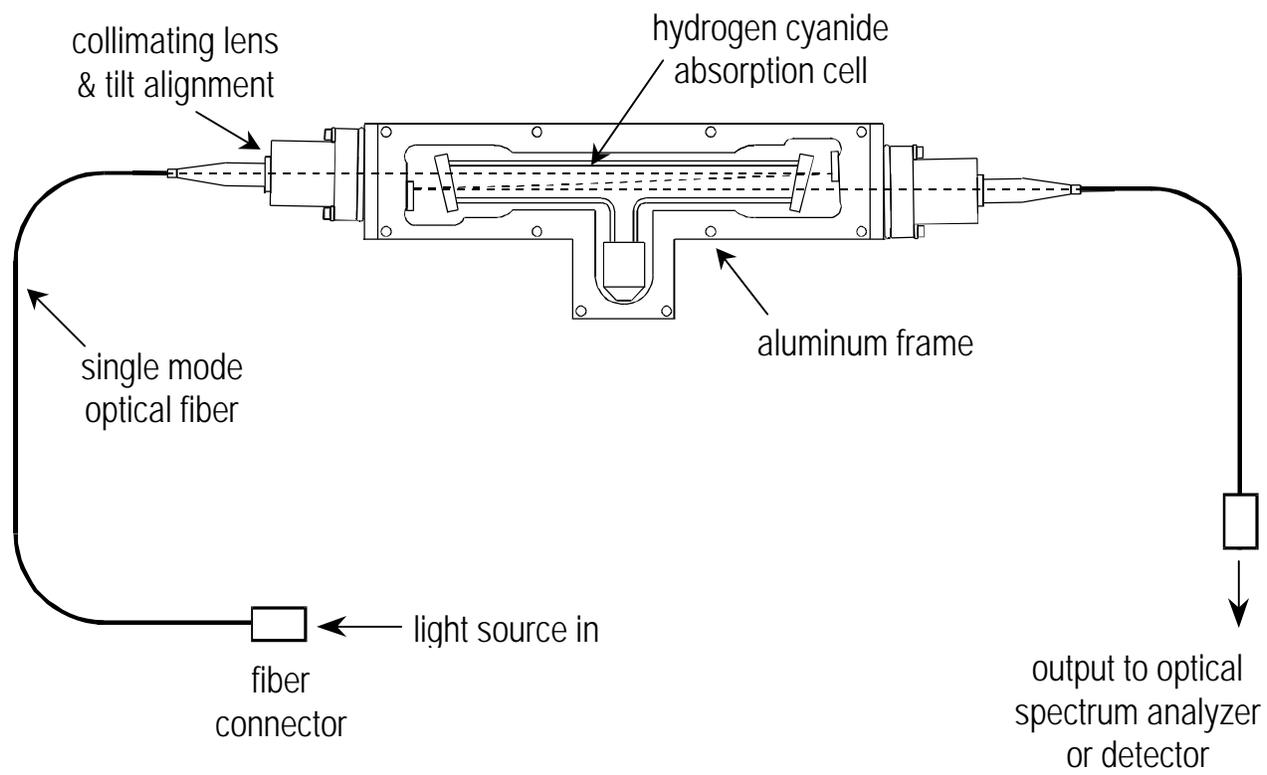


Figure 2. Schematic of fiber-pigtailed SRM cell holder.

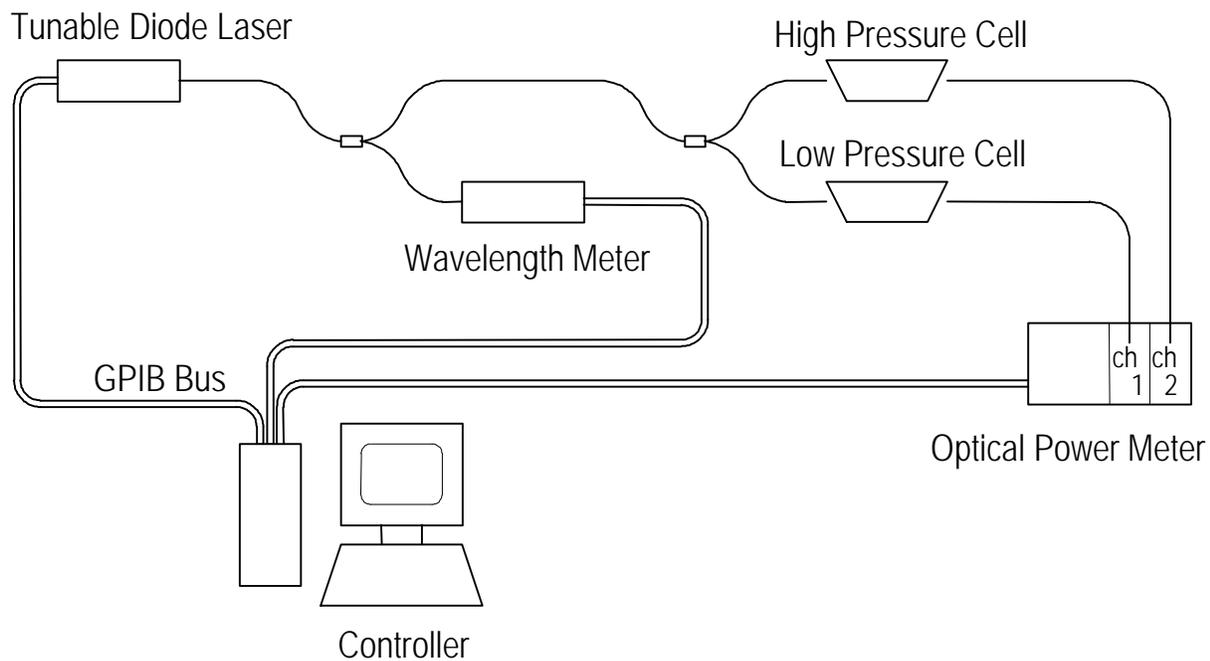


Figure 3. Schematic of the pressure-shift measurement apparatus.

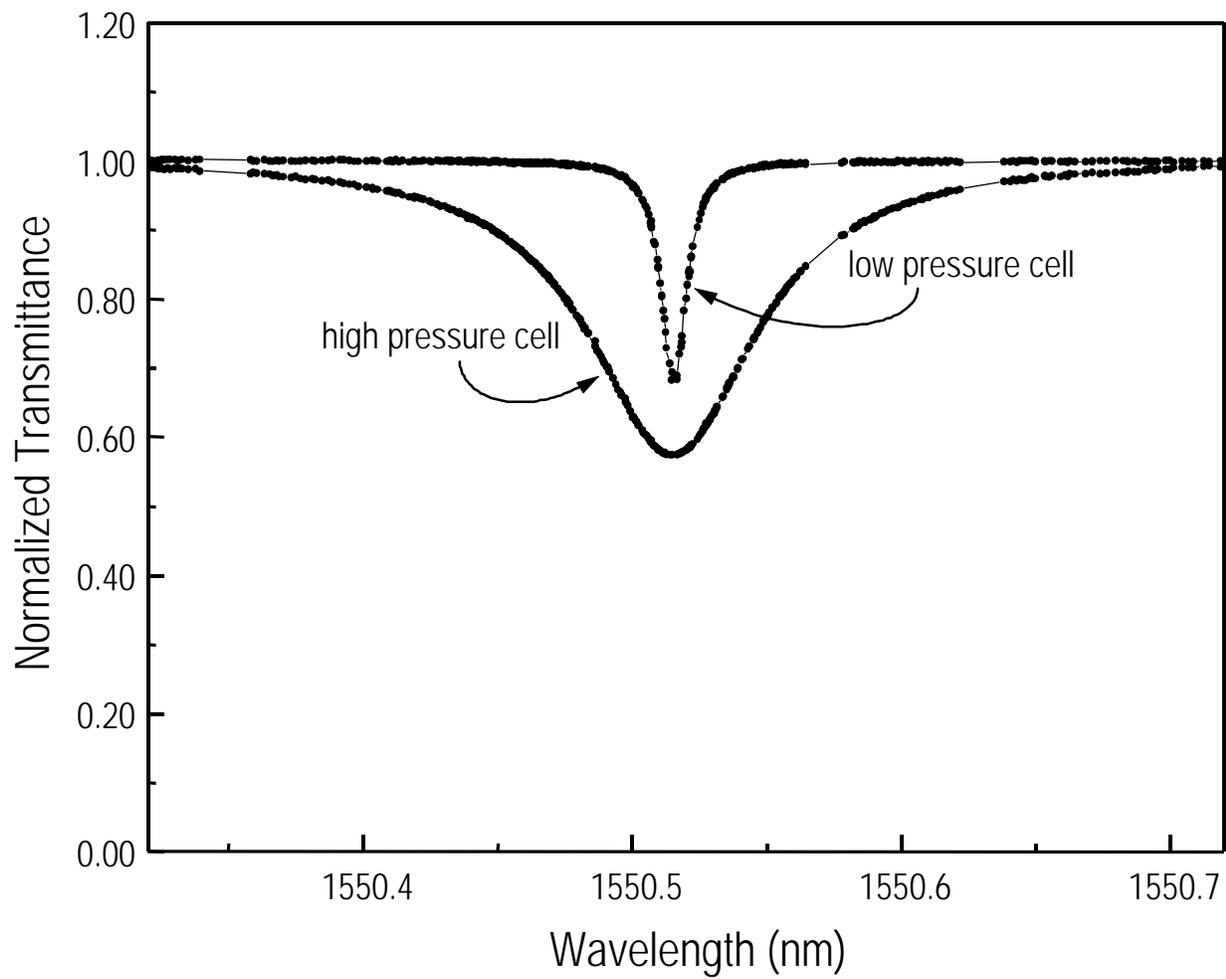


Figure 4. Scan over line P11 showing transmission through low pressure and high pressure cells.

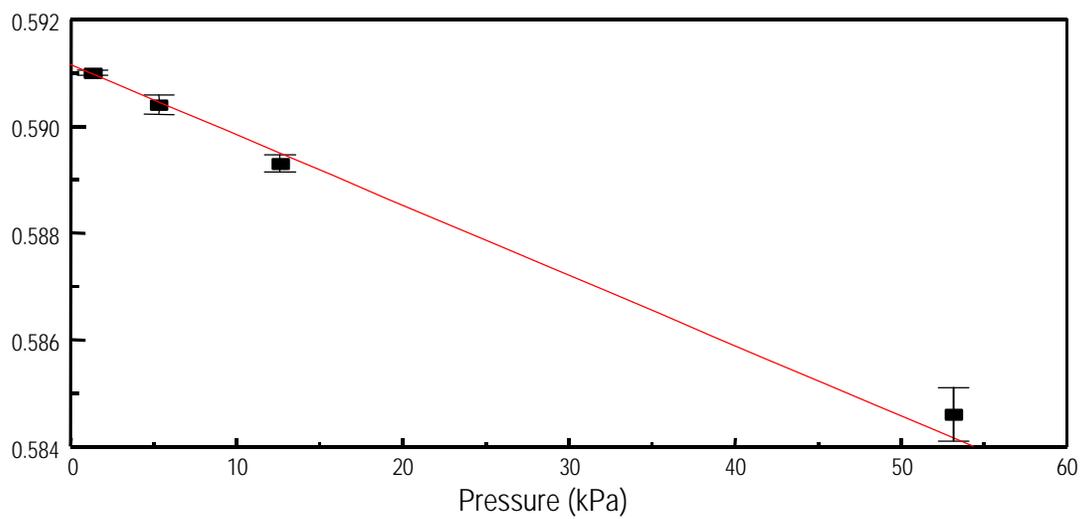
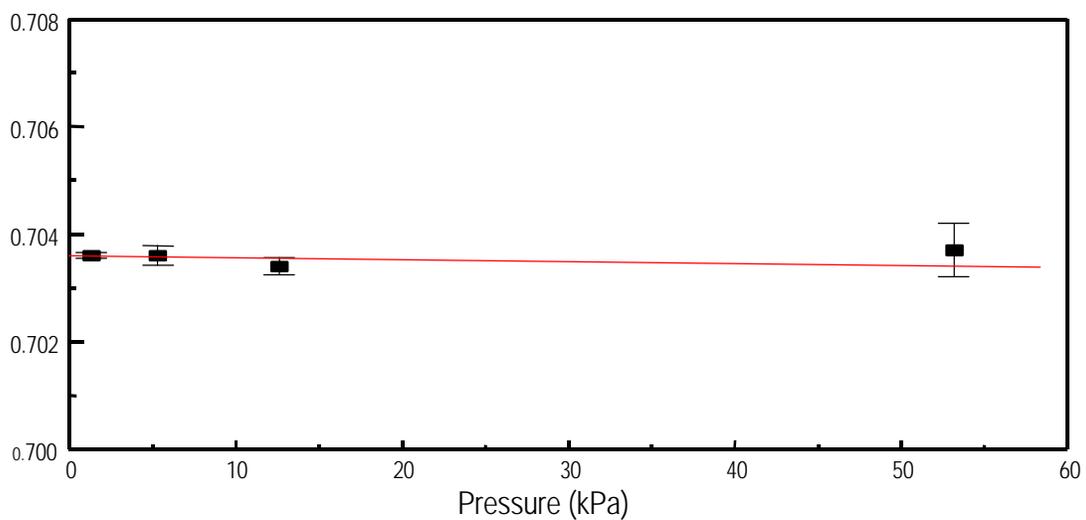
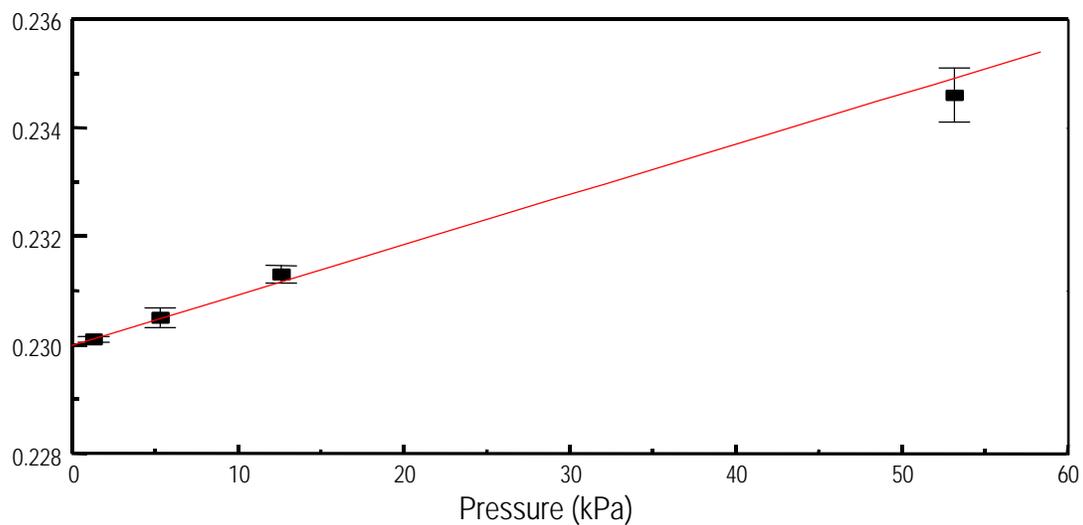


Figure 5. Shift of line centers vs. pressure for lines P4, R8, and P16.

Appendix A. SRM 2519 certificate
(see next six pages)

National Institute of Standards & Technology

Sample Certificate

Standard Reference Material[®] 2519

Wavelength Reference Absorption Cell – Hydrogen Cyanide ($\text{H}^{13}\text{C}^{14}\text{N}$)

Serial No.: SAMPLE

This Standard Reference Material (SRM) is intended for use in calibrating the wavelength scale of wavelength measuring equipment in the spectral region from 1528 nm to 1563 nm. SRM 2519 is an optical-fiber-coupled absorption cell containing hydrogen cyanide ($\text{H}^{13}\text{C}^{14}\text{N}$) gas. Hydrogen cyanide has more than 50 accurately measured absorption lines in the 1500 nm wavelength region.

Certified Wavelength Values: The vacuum wavelengths of absorption lines in the R and P branch of the $2\nu_3$ rotational-vibrational band of $\text{H}^{13}\text{C}^{14}\text{N}$ have been measured previously to high accuracy [1]. NIST has measured the line centers and pressure-induced shifts of 21 lines and certify their wavelengths with an expanded uncertainty (coverage factor $k = 2$) of ± 0.0006 nm. The remainder of the lines in the band are certified with an expanded uncertainty of ± 0.003 nm, where the uncertainty is dominated by the pressure shift uncertainty. Details of the measurement procedure and data analysis for the determination of the pressure shift can be found in reference [2]. A spectrum of the absorption band is shown in Figure 1 and certified wavelength values are given in Table 1. Figure 2 shows a higher resolution scan near lines P10 and P11.

Expiration of Certification: The certification of this SRM is indefinite within the measurement uncertainties specified, provided the SRM is handled, stored, and used in accordance with the instructions given in this certificate.

Measurement Conditions and Procedure: The long term stability of hydrogen cyanide and the use of fundamental molecular absorption lines render the SRM insensitive to changes in environmental conditions. The purpose of the certification procedure is to verify that the unit contains the correct pressure of $\text{H}^{13}\text{C}^{14}\text{N}$ gas and has no significant contaminants that produce additional absorption lines. Measurements were made using a 0.05 nm resolution optical spectrum analyzer. Spectra similar to those shown in Figures 1 and 2 were taken of each SRM unit and compared with measurements of reference absorption cells maintained at NIST. High resolution scans using a tunable laser and wavelength meter were made on at least one unit of each production run. These scans serve to verify the center wavelength of a selected line with an expanded uncertainty of less than ± 0.0006 nm.

Storage and Handling: The protective caps provided for the FC/PC fiber connectors should be replaced when the SRM is not in use. This SRM is intended to be used in a laboratory environment near ambient room temperature ($22\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$). Optical alignment is critical; the user should avoid exposing the unit to large temperature variations, temperature cycling, or mechanical shock, as these may cause the optical alignment to degrade. Optical misalignment affects the throughput of the SRM but will not shift the centers of the absorption lines. A more serious, but less likely problem is cell breakage or leakage. The unit should be replaced if the linewidths or depths differ significantly from those shown in Figures 1 and 2 (when measured using comparable resolution).

Development of the SRM and supporting measurements were performed by S.L. Gilbert and W.C. Swann of the NIST Optoelectronics Division.

Statistical consultation was provided by C.M. Wang of the NIST Statistical Engineering Division.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by J.W.L. Thomas.

Gaithersburg, MD 20899
Certificate Issue Date: September 1998

Thomas E. Gills, Chief
Standard Reference Materials Program

Table 1. Certified Wavelengths for SRM 2519

The table lists the vacuum wavelengths of line centers in the $\text{H}^{13}\text{C}^{14}\text{N } 2\nu_3$ band for the 13.3 kPa (100 Torr) SRM cell pressure. The 21 lines that were measured at NIST are certified with an expanded uncertainty (coverage factor $k = 2$) of ± 0.0006 nm. These lines are shown in the table with a (6) indicating the uncertainty in the last digit. The remaining line centers listed are the literature values from Reference [1]. These values are certified with an expanded uncertainty of ± 0.003 nm, where the uncertainty is dominated by the pressure shift uncertainty.

R Branch	wavelength (nm)	P Branch	wavelength (nm)
25	1528.054	1	1543.1148(6)
24	1528.4862(6)	2	1543.809
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21	1529.8376(6)	5	1545.9563(6)
20	1530.306	6	1546.690
19	1530.786	7	1547.435
18	1531.2764(6)	8	1548.190
17	1531.774	9	1548.9554(6)
16	1532.283	10	1549.7302(6)
15	1532.8024(6)	11	1550.5149(6)
14	1533.329	12	1551.311
13	1533.867	13	1552.116
12	1534.4159(6)	14	1552.931
11	1534.972	15	1553.756
10	1535.5401(6)	16	1554.5892(6)
9	1536.1170(6)	17	1555.4346(6)
8	1536.7034(6)	18	1556.292
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6	1537.907	20	1558.033
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4	1539.149	22	1559.814
3	1539.786	23	1560.7185(6)
2	1540.431	24	1561.6344(6)
1	1541.087	25	1562.563
0	1541.753		

INSTRUCTIONS FOR USE

General Considerations: The SRM can be used to calibrate a wavelength measuring instrument in the 1530 nm to 1560 nm region. The wavelength calibration is vacuum wavelength; if the user requires the wavelength in air, the appropriate correction for the index of refraction of air must be applied (see Reference [3]). Depending on what type of instrument is being calibrated, a broadband source or a tunable narrowband source may be used.

Use With a Broadband Source: A broadband source in the 1500 nm region (such as a light emitting diode, white light, or amplified spontaneous emission source) is useful when calibrating a low resolution instrument such as a diffraction grating based optical spectrum analyzer or monochromator. A schematic for this type of calibration is shown in Figure 3(a). Light from the broadband source is coupled into the SRM and the output (transmission through the SRM) is connected to the instrument that is being calibrated. The absorption lines of hydrogen cyanide appear as dips in the spectrum of the light source (see Figure 1).

Use With a Narrowband Source: The SRM can be used to calibrate the wavelength scale of a tunable narrowband source in this region (such as a diode laser or fiber laser). Alternatively, a tunable source and the SRM can be used to check the calibration of a wavelength meter, as shown in Figure 3(b). The laser is tuned over one or more of the hydrogen cyanide absorption lines. The transmission through the SRM is monitored by a detector; the transmitted power passes through a minimum at the center of an absorption line.

Suggested Procedure for Low-Accuracy Requirements; Calibration Uncertainty > 0.1 nm: Connect the light source (either broadband or narrowband, as discussed above) to one of the fiber connectors on the SRM unit using a single-mode optical fiber terminated with a clean FC/PC connector. After identifying the absorption lines by comparing to the spectrum in Figure 1, find the center or the minimum point of a line listed in Table 1. If the instrument has variable resolution, it is best to use a resolution of ≤ 0.2 nm. For this level of accuracy, the procedure used to find the line center can be quite simple: setting a cursor to the line center or minimum by eye is sufficient. If using a tunable source, simply tune it to the transmission minimum of the line, using tuning steps of ≤ 0.01 nm. Calibrate the instrument to the wavelength of this line (from Table 1) using the calibration procedure specified by the instrument manufacturer. The instrument's linearity can be checked by repeating the procedure for a different absorption line and comparing it to the value listed in Table 1.

Suggested Procedure for Moderate-Accuracy Requirements; Calibration Uncertainty in the Approximate Range of 0.01 nm to 0.1 nm: Connect the light source (either broadband or narrowband, as discussed above) to one of the fiber connectors on the SRM unit using a single-mode optical fiber terminated with a clean FC/PC connector. If the source power varies significantly with wavelength, divide the SRM transmission spectrum by the source spectrum to obtain a normalized trace. After identifying the absorption lines by comparing to the spectrum in Figure 1, make a high resolution scan of a line listed in Table 1. If the instrument has variable resolution, it is best to use a resolution of ≤ 0.1 nm with a data point density of at least one point every 0.005 nm. Find the wavelength readings on both sides of the line where the absorption is 50 % of the maximum; the line center is half-way between these two wavelength readings. Repeat this procedure five times and take the average of the five measurements for the line center. Calibrate the instrument to the center wavelength of this line (from Table 1) using the calibration procedure specified by the instrument manufacturer. The instrument's linearity can be checked by repeating the procedure for a different absorption line and comparing it to the value listed in Table 1.

Suggested Procedure for High-Accuracy Requirements; Calibration Uncertainty < 0.01 nm: *[Note: due to the presence of weak nearby lines and background slope, this SRM is not recommended for a calibration with an uncertainty of less than 0.001 nm.]* Connect the light source (either broadband or narrowband, as discussed above) to one of the fiber connectors on the SRM unit using a single-mode optical fiber terminated with a clean FC/PC connector. Divide the SRM transmission spectrum by the source spectrum to obtain a normalized trace. After identifying the absorption lines by comparing to the spectrum in Figure 1, make a high resolution scan of a line listed in Table 1. If the instrument has variable resolution, it is best to use a resolution of ≤ 0.1 nm with a data point density of at least one point every 0.001 nm. Using a fitting technique such as the least squares technique, fit the absorption data to the appropriate lineshape (Lorentzian if the line shape is dominated by the molecular absorption profile, Lorentzian convoluted with the instrument's filter characteristics if the instrument contributes significantly to the profile). Details of line fitting procedure and potential error sources can be found in Reference [2]. Calibrate the instrument to the center wavelength of this line (from Table 1) using the calibration procedure specified by the instrument manufacturer. The instrument's linearity can be checked by repeating the procedure for a different absorption line and comparing it to the value listed in Table 1.

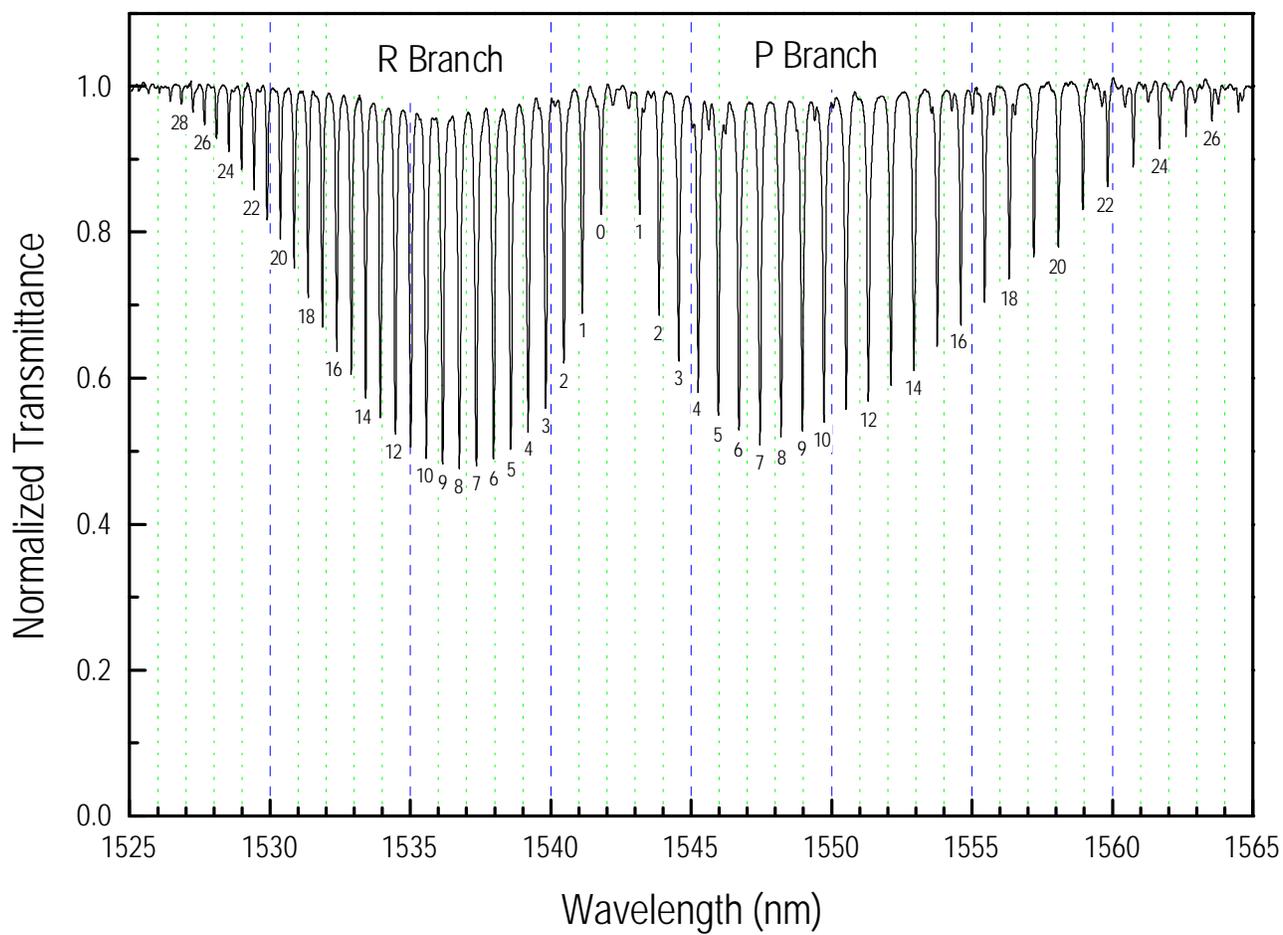


Figure 1. Hydrogen cyanide (H¹³C¹⁴N) spectrum taken by passing LED light through a SRM unit and recording the spectrum of the transmitted light using an optical spectrum analyzer with 0.05 nm resolution. The figure shows the recorded spectrum divided by the LED spectrum. The HCN gas pressure is 13 kPa and the optical path length through the gas is 22.5 cm.

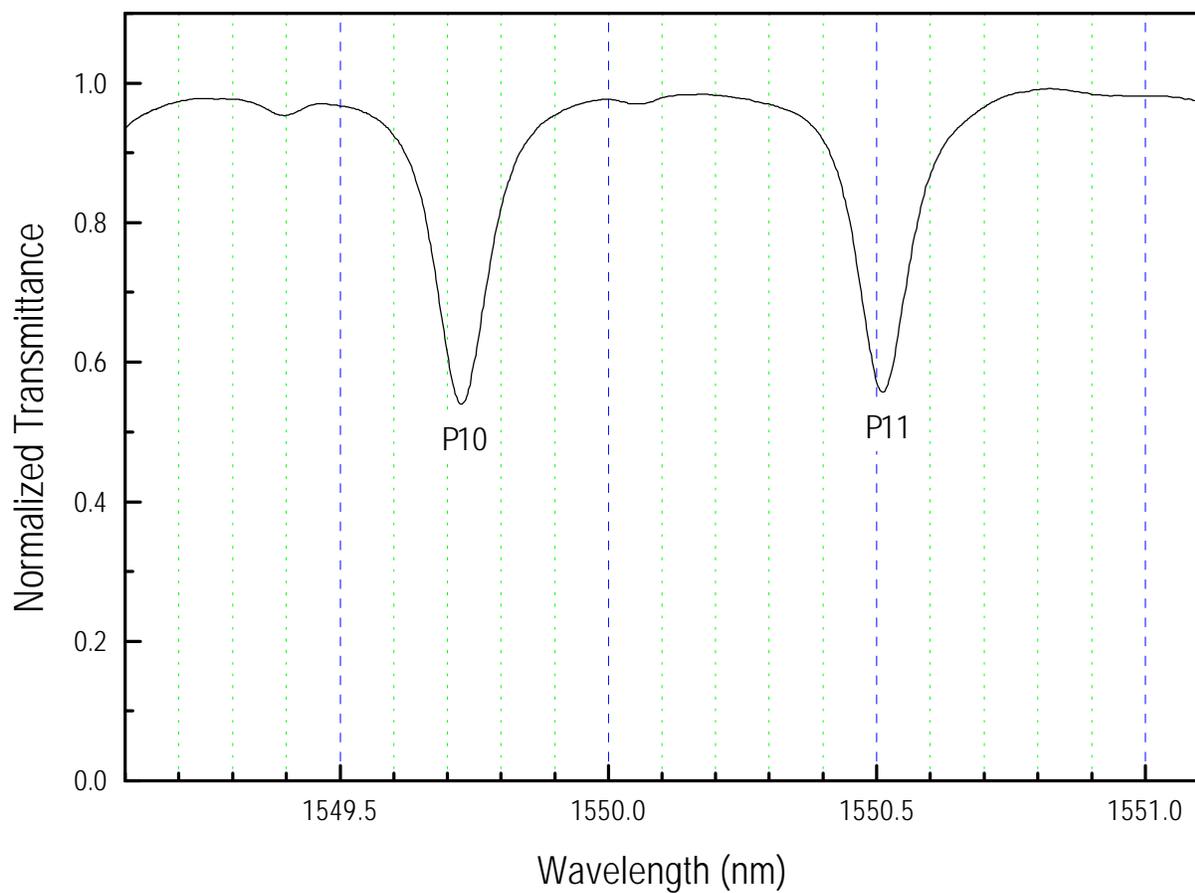


Figure 2. The P10 and P11 lines from Figure 1 on an expanded wavelength scale to show lineshape.

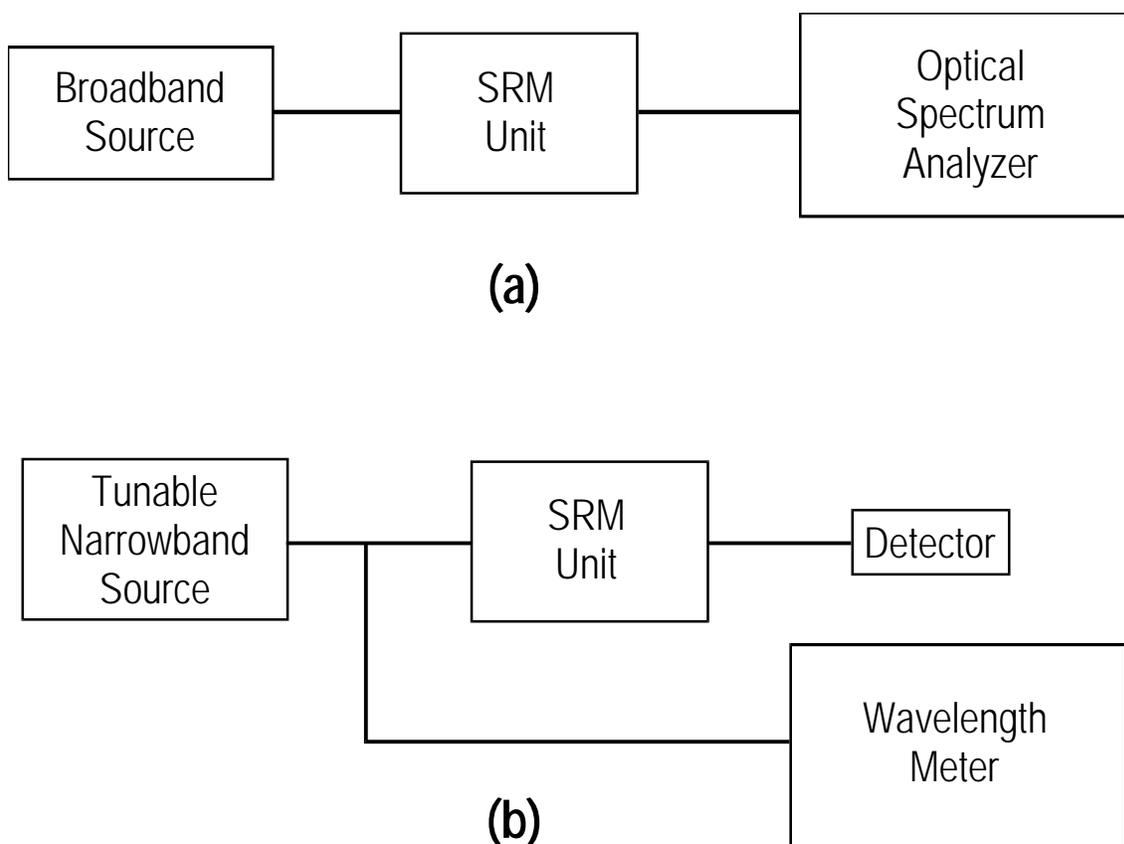


Figure 3. (a) Schematic of technique when using the SRM and a broadband source to calibrate an optical spectrum analyzer. (b) Schematic of technique when using the SRM and a narrowband source to calibrate a tunable laser or a wavelength meter. The wavelength meter is not required for a laser calibration.

REFERENCES

- [1] H. Sasada and K. Yamada, "Calibration lines of HCN in the 1.5- μ m region," *Appl. Opt.* **29**, 3535-3547 (1990).
- [2] Gilbert, S.L., Swann, W.C., and Wang, C.M., "Standard Reference Materials: Hydrogen Cyanide H¹³C¹⁴N Absorption Reference for 1530–1560 nm Wavelength Calibration – SRM 2519," NIST Special Publication 260-137 (1998).
- [3] Edlen, B., "The Refractive Index of Air," *Metrologia*, **2**, p. 12, (1966); *CRC Handbook of Chemistry and Physics 77th Ed.*, pp. 10-266, (1996).

It is the responsibility of users of this SRM to assure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at (301) 975-6776 (select "Certificates"), Fax (301) 926-4751, e-mail srminfo@nist.gov, or via of the Internet <http://ts.nist.gov/srm>.